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(56) Documents Cited
GB 1475500 A GB 1290608 A GB 0916542 A
EP 0719740 A

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(54) Lead-free crown glass

(57) Lead-free crown glass having a Refractive Index of between 1.49 and 1.54 and Abbé coefficient of between 55 and 62 and having the following composition (in % by weight based on oxides): SiO_2 60 - 75, B_2O_3 0 - 8; Na_2O 0 - 12, K_2O 0 - 25 with $Na_2O + K_20$ 12 - 25, GaO 0 - <5, ZnO 3 - 15, TiO_2 0 - <1 and ZrO_2 0 - 3.

GB 2 320 023 A

Lead-free crown glass

The invention relates to lead-free crown glass which have refractive indices n_d of between 1.49 and 1.54 and Abbe coefficients ν_d of between 55 and 62.

Since, in recent years, the glass components PbO and As_2O_3 have come to be widely considered (and to public discussion) as pollutants of the environment, there is also a trend towards using glass which is free of PbO, and also free of As_2O_3, in optical instruments. Therefore, such glass having the specific optical properties, for example with respect to refractive index, Abbe coefficient and also transmission, should be available on the market.

Reproducing all the desired optical and also glass (-technical) properties affected by the lead oxide by simple replacement of the PbO by one or more other constituents is as a rule unsuccessful. Rather, new developments in the glass composition are necessary in most cases. Specifications in which lead-free crown flint glass or crown glass is described are already to be found in the patent literature . However, this glass still has extremely wide-ranging disadvantages.

German Patent Specification DE 973,350 describes glass which can be lead-free but always contains fluorine in order to lower the refractive index. The same applies to the glass from JP 1-133,956 A. As regards the environmental protection idea already mentioned, the use of this component should strictly be avoided as well, since, under some circumstances, harmful emissions of fluorine can occur during the smelting process.

The glass described in British Patent Specification GB 2,029,401 B contains up to 20% by weight of CaO. However, the introduction of CaO, in particular in relatively large quantities, lowers the viscosity at high temperatures, but increases it at low temperatures; that is to say the viscosity/temperature curve becomes steeper, the addition of CaO thus making the glass shorter.

European Patent Specification EP 0,151,346 B1

mentions crown glass which requires high B_2O_3 contents for reducing the melting temperatures and high TiO_2 contents for reaching the refractive index and for adjusting the UV edge and which must contain As_2O_3. TiO_2 considerably reduces the UV transmission. However, TiO_2, in particular in relatively large proportions, can lead to undesirable coloration of the glass. The disadvantages resulting from the high TiO_2 content also exist in the case of glass from German Auslegeschrift DE-AS 1,050,965, which contains up to 8% by weight of TiO_2.

As in the glass from EP 0,151,346 B1, Al_2O_3 is also a necessary constituent described in the crown glass in JP 4-40,301 B2 and JP 4-70,262 B2 (up to 10 and 15 or 14% by weight respectively). Such glass will show a heightened tendency to devitrification.

JP 6-107,425 A describes glass whose optical properties vary over a wide range and which necessarily contains BaO (up to 45% by weight) and Nb_2O_5 (up to 25% by weight). The use of the last-mentioned, expensive component enormously increases the price of the mixture. The low SiO_2 contents of the glass are compensated by relatively high proportions of B_2O_3, which allows the conclusion that the chemical resistance of the glass is not very high.

It is the object of the invention to provide lead-free crown glass having a refractive index n_d of between 1.49 and 1.54 and an Abbe coefficient ν_d of between 55 and 62, which has a high light transmission in the wavelength range between 380 nm and 700 nm and is readily fusible and processable and can be produced cost-effectively.

This object is achieved by the glass described in Patent Claim 1.

The glass belongs to an SiO_2-M_2O-ZnO glass system in which SiO_2 functions as a network former. SiO_2 is present in proportions from 60 to 75% by weight. It can, however, be replaced by up to 8% by weight of B_2O_3. As a result, the melting temperatures are reduced. In the case of higher proportions of B_2O_3, the chemical resistance

would be reduced and segregations would occur in the glass.

To lower the melting temperatures, the glass contains Na_2O (0 - 12% by weight) and/or K_2O (0 - 25% by weight), the total of these two components being at least 12% by weight, in order to reduce the melting temperatures sufficiently, and being at most 25% by weight, so as not to cause the high chemical resistance of the glass to deteriorate. Furthermore, the glass can contain up to 2% by weight each of Li_2O and Cs_2O, but even then the total of the alkali metal oxides should not exceed 25% by weight (Na_2O + K_2O + Li_2O + Cs_2O 12 - 25% by weight).

To achieve the said optical properties, the glass contains 3 - 15% by weight of ZnO. In order to keep the ZnO content low in the case of the desired data, the glass can also contain TiO_2 (0 - <1% by weight) and ZrO_2 (0 - 3% by weight). Higher TiO_2 contents lead to transmission losses in the UV range, and higher ZrO_2 contents raise the melting temperatures. Preferably, the total of TiO_2 and ZrO_2 in the glass is at least 0.1% by weight. It is particularly preferred for the glass to contain at least 0.1% by weight of TiO_2. This is because TiO_2 has a more pronounced effect on the Abbe coefficient than ZnO, and an unduly high ZnO content would reduce the devitrification stability.

For a modification of the optical position, up to 3% by weight of Nb_2O_5, up to 3% by weight of Ta_2O_5 and up to 3% by weight of WO_3 can also be added to the glass according to the invention, but this entails a higher cost of the mixture owing to the high price of these components.

Furthermore, the glass can contain up to less than 5% by weight of CaO. This component advantageously improves the chemical resistance and the processability. With higher proportions, however, there is a risk of the optical properties no longer being achieved.

In addition, the glass can also contain up to 3% by weight each of BaO, SrO and MgO, without the melting and processing properties being substantially changed.

However, MgO at least in relatively high proportions, diminishes the devitrification stability of the glass, so that this component is omitted in most cases.

Within the range claimed in the main claim, there are two separate preferred glass composition regions which, with their refractive indices and Abbe coefficients, each replace a commercially available lead-containing glass type.

On the one hand, this is the high-CaO and high-ZnO composition region (in % by weight based on oxides) with SiO_2 65 - 70, B_2O_3 2 - 6, Na_2O 3 - 8, K_2O 9 - 14, CaO 1 - 4, TiO_2 0 - <1, ZnO 7 - 11 and ZrO_2 0 - 1.

On the other hand, this is the high-K_2O and low-ZnO composition region (in % by weight based on oxides) with SiO_2 66 - 70, B_2O_3 2 - 5, Na_2O 5 - 8, K_2O 15 - 18 with $Na_2O + K_2O \leq 25$, CaO 0 - 1, TiO_2 0 - <1, ZnO 4 - 7 and ZrO_2 0 - 1.

For fining the glass, fining agents known per se can be added to the mixture. If no As_2O_3 is used but, for example, sulphates, chlorides, Sb_2O_3 or CeO_2 are used instead, which is possible without reducing the glass quality, the lead-free glass according to the invention is additionally free of arsenic.

The lead-free optical glass according to the invention, which represents a further group of crown glass having the given refractive indices and Abbe coefficients, is distinguished by high transmission in the wavelength range between 380 nm and 700 nm. The glass is readily fusible and processable and can be produced cost-effectively; it shows high devitrification stability and good chemical resistance.

Examples:

Six examples of glass according to the invention were smelted from conventional raw materials. Their compositions (in % by weight based on oxides) and their refractive indices n_d and their Abbe coefficients ν_d are listed in the table.

Table

Compositions (in % by weight based on oxides) of glass according to the invention:

	1	2	3	4	5	6
SiO_2	67.89	68.59	66.26	69.02	68.35	67.71
B_2O_3	3.21	3.53	3.73	4.49	4.59	4.56
Na_2O	6.96	6.40	6.17	4.59	4.38	4.86
K_2O	16.08	16.15	12.87	10.71	10.14	10.23
ZnO	5.45	5.04	8.16	8.30	9.40	9.61
TiO_2	0.32	0.14	0.32	0.32	0.40	0.45
ZrO_2	0.10	0.14	-	-	-	-
CaO	-	-	2.49	2.58	2.74	2.59
n_d	1.5115	1.5103	1.5213	1.5189	1.5213	1.5220
ν_d	59.43	60.17	59.16	60.16	59.72	59.47

For highlighting the high transmission, the spectral pure transmission ratio at the wavelength of λ = 400 nm and a layer thickness of d = 25 mm may be mentioned: $\tau_{i\ (400\ nm,\ 25\ mm)}$ is 0.991 (Example 2) or 0.995 (Example 6).

CLAIMS

1. Lead-free crown glass having a refractive index n_d of between 1.49 and 1.54 and an Abbe coefficient ν_d of between 55 and 62, characterized by the following composition (in % by weight based on oxides):

SiO_2	60 - 75
B_2O_3	0 - 8
Na_2O	0 - 12
K_2O	0 - 25
with $Na_2O + K_2O$	12 - 25
CaO	0 - <5
ZnO	3 - 15
TiO_2	0 - <1
ZrO_2	0 - 3

and, if appropriate, fining agents in the customary quantities.

2. Crown glass according to Claim 1, characterized in that the total of $TiO_2 + ZrO_2$ is at least 0.1% by weight.

3. Crown glass according to Claim 1 or 2, characterized by the following composition (in % by weight based on oxides):

SiO_2	65 - 70
B_2O_3	2 - 6
Na_2O	3 - 8
K_2O	9 - 14
CaO	1 - 4
ZnO	7 - 11
TiO_2	0 - <1
ZrO_2	0 - 1

and, if appropriate, fining agents in the customary quantities.

4. Crown glass according to Claim 1 or 2, characterized by the following composition (in % by weight based on oxides):

SiO_2	66 - 70
B_2O_3	2 - 5
Na_2O	5 - 8
K_2O	15 - 18

with $Na_2O + K_2O$	≤25
CaO	0 - 1
ZnO	4 - 7
TiO_2	0 - <1
ZrO_2	0 - 1

and, if appropriate, fining agents in the customary quantities.

5. Crown glass according to at least one of Claims 1 to 4, characterized in that it additionally contains:

Li_2O	0 - 2
Cs_2O	0 - 2
with $Na_2O + K_2O + Li_2O + Cs_2O$	≤25
MgO	0 - 3
SrO	0 - 3
BaO	0 - 3
Nb_2O_5	0 - 3
Ta_2O_5	0 - 3
WO_3	0 - 3

6. Crown glass according to at least one of Claims 1 to 5, characterized in that, apart from unavoidable contaminations it is free of arsenic oxide.

The Patent Office

4

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Claims searched: 1-6 **Date of search:** 12 January 1998

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C1M (MAG)

Int Cl (Ed.6): C03C 3/078

Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage			Relevant to claims
X	GB 1475500	PILKINGTON	glass 91	1,2 at least
X	GB 1290608	PHILIPS	example 9	1 at least
X	GB 0916542	BAUSCH & LOMB	claim1	1 at least
X	EP 0719740 A	CORNING FRANCE	examples 2-6	1,2 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.